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Long-Term and Seasonal Changes in Sources of Urban Atmospheric Particulates in the Western Pacific

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Abstract: To reduce atmospheric pollutants, the sources need to be identified. To this end, combustion-derived particulates (P_c) in atmospheric suspended particulate matter (TSP) in ten Western Pacific cities from 1997 to 2018 were analyzed using the NP method, which we have recently developed. The method separates P_c into particulates originating from high-temperature (P_h) and low-temperature (P_l) combustion sources. Using this method, ten cities in the Asia-Pacific region were separated into three classes. Class 1: commercial cities whose major contributor to P_c was from vehicles, and which showed lower [P_c] values with larger [P_h]/[P_c] ratios. Sapporo, Kanazawa, Tokyo, Sagamihara (Japan), Shanghai (China), and Busan (Korea) were contained in this class. Class 2: cities whose main source of P_c was from coal heating, and which showed much higher winter [P_c] with larger [P_l]/[P_c] ratios. Beijing, Shenyang (China), and Vladivostok (Russia) were contained in this class. Class 3: steel manufacturing city which showed lower [P_c] with larger [P_l]/[P_c] ratio. The low [P_c] appeared to be due to elimination of P_l from coke oven plants. Only Kitakyushu was contained in this class. This study has elucidated the contribution of sources to urban atmospheric TSP in the Western Pacific that was previously unknown. Overall [P_c] was decreasing in this region, mainly due to the decreasing contribution of vehicles to P_c, but not due to a decrease in coal combustion.

Keywords: combustion-derived particulate; vehicle emission; coal combustion; Western Pacific; NP method

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1. Introduction

Air pollution kills millions of people every year, especially in African, south-east Asian, eastern Mediterranean, and Western Pacific regions [1]. Among airborne particulate matter (PM) of various sizes, finer inhalable particles with diameters that are generally 2.5 μm and smaller ($PM_{2.5}$) have attracted research attention, as they are implicated in respiratory and cardiovascular diseases. The incomplete combustion of organic materials produces many types of polycyclic aromatic hydrocarbons (PAHs). In the air, PAHs with four or more rings, such as the carcinogenic benzo[*a*]pyrene, exist mostly as being adsorbed to PM. Combustion also produces nitropolycyclic aromatic hydrocarbons (NPAHs), formed by the nitration of PAHs. Although combustion is the primary source for NPAHs, several NPAHs are formed secondarily in the atmosphere. NPAHs with four or more rings exist mostly as being adsorbed to PM [2,3]. NPAHs in particulates warrant research attention since they are more mutagenic than their parent PAHs [4,5]. PAHs and NPAHs are emitted from many combustion sources, including vehicles, motorcycles, factories, power stations, incinerators, heaters and ovens in homes, post-harvest field burning, and forest fires [6].

In general, atmospheric concentrations of NPAHs are at least two orders of magnitude lower than those of PAHs [7–9]. To clarify the current trends in air pollution caused by

PAHs and NPAHs in the Western Pacific, the total suspended particulates (TSP) in 10 cities in Japan, China, Russia, and Korea in both summer and winter have been collected since 1997 [10–12]. In Japan, urban air pollution was serious in the 1980s and 1990s due to the enormous increase in vehicular traffic. This resulted in an increase in respiratory disease patients [13]. To improve air quality, the Japanese government lowered allowable PM and nitrogen oxide (NO_x) emissions from new vehicles. Consequently, the urban atmospheric PAH concentrations and especially NPAH concentrations decreased in many Japanese cities in the 2000s [14–17]. Several cities in central and northern China and far-eastern Russia showed PAH concentrations that were an order or more higher, although the concentration ratios of NPAHs to PAHs were smaller. This suggests that coal combustion was a major pollution source in those regions. PAH concentrations in Chinese cities did not decrease as rapidly as they did in Japanese cities [11]. Thus, vehicle emissions and coal combustion products were major contributors to atmospheric pollution in the Western Pacific countries. However, the fraction in TSP derived from combustion and the contributions of vehicle emissions and coal combustion were not known.

Since the nitration of PAHs is dependent on combustion temperature, ratios of NPAHs to PAHs differ between high-temperature combustion sources, such as vehicles, and low-temperature combustion sources, such as coal combustion. However, contributions of these sources to atmospheric concentrations of PM, PAHs, and NPAHs cannot be obtained by simple NPAH:PAH ratios. Recently, we developed a method, named the NP method, to calculate the contributions of major sources to atmospheric combustion-derived PM, using 1-nitropyrene (1-NP) and pyrene (Pyr), and found its usefulness by using several TSP samples collected in the Western Pacific [18,19]. Here, the method is applied to atmospheric TSP samples collected in 10 cities in this region from 1997 to 2018. This is the first study to estimate the long-term and seasonal changes in contributions from vehicles and coal combustion to combustion-derived particulates in this region.

2. Materials and Methods

2.1. Sampling Cities in the Western Pacific

TSP samples were collected in residential areas in Sapporo, Kanazawa, Tokyo, Sagamihara, and Kitakyushu (Japan), Shenyang, Beijing, and Shanghai (China), Vladivostok (Russia), and Busan (Korea) (Figure S1). Characteristics of these cities (locations, populations, average temperatures, and main industries) are summarized in Table S1. The five Japanese cities in the above list do not consume coal for winter heating. Among them, Kitakyushu is a typical steel manufacturing city, and the others are commercial cities. Among the three Chinese cities, Shenyang and Beijing consume large amounts of coal for winter heating, whereas Shanghai does not. Vladivostok also uses coal for winter heating. Vladivostok and Busan have big ports near their centers, but both sampling sites were more than 5 km away from the ports. In all cities, airports are more than 20 km away from the sampling sites.

In each city, a high-volume air sampler equipped with a quartz fiber filter (8 × 10 inch, 2500QAT-UP, Tokyo Dylec, Tokyo, Japan) was set in a residential area not far from downtown, and 24-h sampling of TSP was continued for two consecutive weeks in the winters and summers from 1997 to 2018.

2.2. Characterization of PAHs and NPAHs

A total of nine PAHs and six NPAHs in the TSP samples were characterized in previous studies [10–12], using HPLC coupled to fluorescence and chemiluminescence detectors (Text S1 in Supplemental Information) [20]. Due to their ubiquity, Pyr and 1-NP were used for the NP-method calculations.

2.3. Source Contribution Calculations

The NP method for calculating combustion source contributions to TSP is briefly described. TSP was divided into combustion-derived particulate matter (P_c) and non-

combustion-derived particulate matter (P_n), and P_c was further divided into particulates from combustion sources with high-temperature (P_h) and low-temperature (P_l). x is defined as $[P_h]/[P_c]$, i.e., the proportion of P_c in the atmosphere due to P_h ($0 < x < 1$), and y as $[P_c]/([TSP])$, i.e., the fraction of TSP in the atmosphere due to P_c ($0 < y < 1$). The atmospheric concentrations of P_c-bound 1-NP ([1-NP]) and Pyr ([Pyr]) are expressed by the following equations:

$$[\text{1-NP}] = [\text{1-NP}_h][P_c]x + [\text{1-NP}_l][P_c](1 - x) \quad (1)$$

$$[\text{Pyr}] = [\text{Pyr}_h][P_c]x + [\text{Pyr}_l][P_c](1 - x) \quad (2)$$

where $[\text{1-NP}_h]$ and $[\text{Pyr}_h]$ are concentration of 1-NP and Pyr in P_h, respectively, and $[\text{1-NP}_l]$ and $[\text{Pyr}_l]$ are the concentrations of 1-NP and Pyr in P_l, respectively. Our previous studies found that the $[\text{1-NP}_h]/[\text{Pyr}_h]$ ratio was nearly constant at 0.425, and the $[\text{1-NP}_l]/[\text{Pyr}_l]$ ratio was nearly constant at 0.0013 [18]. These values were substituted in Equations (1) and (2), since they depend on combustion temperatures of the major sources as described below. Among the P_c sources, only vehicle engines use high combustion temperatures in the range 2700–3000 °C, resulting in a large [1-NP]/[Pyr] ratio. In the Western Pacific, coal, oil, and natural gas are the main energy sources [21]. Among them, coal and oil are used in industry, power production, and heating, especially during the winter. The combustion of coal occurs at temperatures in the range 1100–1200 °C. Due to this relatively low combustion temperature, NPAH formation is lower than with vehicles and therefore the [1-NP]/[Pyr] ratio of coal combustion is comparatively low. Natural gas emits the smallest amount of PM among the above energy sources. Moreover, there was little post-harvest field burning, whose combustion temperature is in the range 500–600 °C, during the air sampling periods in this study [22]. Therefore, vehicle emissions and coal combustion were respectively used as representative combustion sources with high and low temperatures.

Atmospheric concentrations of TSP, Pyr, and 1-NP were obtained (Table S2) from previous studies [10–12], and were used to calculate the source contribution parameters x and y in the above equations. Using the definitions $x = [P_h]/[P_c]$ and $y = [P_c]/[TSP]$, $[P_c]$, $[P_n]$, $[P_h]$ and $[P_l]$ were obtained.

3. Results and Discussion

3.1. Individual City Trends

Table S3 shows the fraction of P_h in the atmospheric P_c (=x) and the fraction of P_c in the atmospheric TSP (=y) in the 10 cities in the summer and winter from 1997 to 2018, which were calculated by equations of the NP-method using [TSP], [1-NP], and [Pyr] in Table S2. Table 1 shows $[P_c]$, $[P_h]$, and $[P_l]$ in the same samples, which were calculated by using the x and y values in Table S3 and [TSP] in Table S2. In order to know seasonal differences, summer, winter, and annual concentrations of $[P_c]$ in 10 cities are shown in Table 2 with the winter/summer ratio. In order to compare combustion sources, annual concentrations of $[P_h]$ and $[P_l]$ in 10 cities are shown in Table 3 with the $[P_h]/[P_c]$ ratio. In these tables, Tokyo was combined with Sagamihara, a suburb of Tokyo.

The data in Table 2 shows that the Japanese cities had much lower annual $[P_c]$ values (less than 2 μg m^{-3}) than the cities in the other countries. The $[P_h]/[P_c]$ ratios (=x) of these cities were greater than 0.70, except for Kitakyushu, where the ratio was 0.34. Figure 1 shows the variations of [TSP] and $[P_c]$ in Kanazawa as typical to those in Japanese commercial cities. $[P_c]$ was over 10 μg m^{-3} in the winter of 1999 with larger $[P_c]/[TSP]$ ratio (y = 0.2, Table S3) than those in the other Japanese cities. However, $[P_c]$ started to decrease in the 2000s, and did not exceed 1 μg m^{-3} by the winter of 2018. The seasonal change (summer < winter) in $[P_c]$ was larger than that found with [TSP] [23]. The fraction of $[P_h]$ in $[P_c]$ decreased, and was less than one-third in the winter of 2018, although the average $[P_h]/[P_c]$ ratio (=x) was 0.8 (Table 3). The same decreasing tendency in the $[P_h]/[P_c]$ ratio was observed in Sapporo and Tokyo/Sagamihara, although the decrease of $[P_c]$ was very slight (Table 1). Since the Japanese cities in this study with the exception of Kitakyushu are

commercial cities, these results suggest that the main contributor to P_c was vehicles, and that these contributions are decreasing.

Table 1. $[P_c]$, $[P_h]$ and $[P_l]$ ($\mu g\ m^{-3}$) in 10 cities in summers (S) and winters (W) from 1997 to 2018.

Year/Season	$[P_c]$	$[P_h]$	$[P_l]$
	Sapporo		
1997 S	-	-	-
1997 W	-	-	-
2004 S	0.5	0.33	0.17
2005 W	1.9	1.37	0.53
2007 S	0.37	0.294	0.076
2008 W	3.4	2.24	1.16
2010 S	0.22	0.16	0.06
2010 W	1.8	1.06	0.74
2013 S	0.11	0.054	0.056
2014 W	0.9	0.64	0.26
	Kanazawa		
1997 S	-	-	-
1997 W	-	-	-
1999 S	3	2.8	0.2
1999 W	11.1	10.49	0.51
2004 S	1.6	1.43	0.17
2005 W	2.3	2	0.3
2007 S	0.8	0.67	0.13
2008 W	1.2	0.74	0.46
2010 S	0.3	0.2	0.1
2010 W	1.1	0.6	0.5
2013 S	0.4	0.27	0.13
2014 W	0.9	0.34	0.56
2017 S	0.18	0.071	0.1
2018 W	0.47	0.16	0.31
	Tokyo		
1997 S	-	-	-
1997 W	-	-	-
2004 S	0.41	0.26	0.15
2005 W	0.84	0.74	0.1
	Sagamihara		
2007 S	0.32	0.32	0.003
2008 W	0.42	0.23	0.19
2010 S	0.068	0.01	0.058
2010 W	0.91	0.41	0.5
2013 S	0.38	0.24	0.14
2014 W	0.78	0.69	0.09
	Kitakyushu		
1997 S	-	-	-
1997 W	-	-	-
2004 S	1.2	0.29	0.91
2005 W	1.6	1.05	0.55
2007 S	0.15	0.08	0.07
2008 W	0.9	0.38	0.52
2010 S	0.4	0.17	0.33
2010 W	1.1	0.51	0.59
2013 S	0.12	0.02	0.01
2014 W	2.8	0.29	2.51
	Shenyang		
2001 S	3	2.24	0.76
2002 W	78.6	5.9	72.7
2007 S	4.5	2.45	2.05

Table 1. *Cont.*

Year/Season	$[P_c]$	$[P_h]$	$[P_l]$
2008 W	31.1	10.6	20.5
2010 S	32.2	21.4	10.8
2010 W	20.7	10.3	10.4
2013 S	3	1.28	1.72
2014 W	41.1	9.3	31.8
	Beijing		
2004 W	57.1	7.9	49.2
2007 S	2.3	1	1.3
2008 W	37.3	8.3	29
2010 S	1.3	0.6	0.7
2010 W	86.9	0.7	86.2
2013 S	1.1	0.4	0.7
2014 W	26	2.3	23.7
	Shanghai		
2007 S	2.5	2.3	0.2
2007 W	3	2.3	0.7
2010 S	0.73	0.53	0.2
2010 W	4.5	3	1.5
2013 S	0.48	0.28	0.2
2014 W	2.6	1	1.6
2015 S	-	-	-
2015 W	-	-	-
2017 S	-	-	-
2018 W	-	-	-
	Vladivostok		
1999 S	-	-	-
1999 W	-	-	-
2005 W	-	-	-
2007 S	0.48	0.26	0.22
2008 W	12.5	4.8	7.7
2010 S	0.53	0.26	0.27
2010 W	19.3	4.1	15.2
2013 S	0.15	0.08	0.07
2014 W	4.3	2.1	2.2
	Busan		
2005 W	1.9	1.2	0.7
2007 S	0.37	0.28	0.09
2008 W	2.4	1.3	1.1
2010 S	0.34	0.18	0.16
2010 W	2.2	0.8	1.4

$[P_c]$ was calculated from y and both $[P_h]$ and $[P_l]$ were calculated from x in Table S3. Blank means not calculated.

Table 2. Annual, summer, and winter $[P_c]$ ($\mu g\ m^3$) in 10 cities with winter/summer ratios.

City	$[P_c]$			Winter/Summer
	[a] Annual	Summer	Winter	
Sapporo	1.15 ± 1.14	0.30 ± 0.17	2.00 ± 1.00	6.7
Kanazawa	1.94 ± 3.00	1.05 ± 1.09	2.85 ± 4.09	2.7
Tokyo/Sagamihara	0.52 ± 0.29	0.29 ± 0.16	0.74 ± 0.22	2.6
Kitakyushu	1.03 ± 0.89	0.47 ± 0.50	1.60 ± 0.58	3.4
Shenyang	26.78 ± 25.64	10.68 ± 14.37	42.88 ± 25.23	4.0
Beijing	30.29 ± 32.83	1.57 ± 0.64	51.80 ± 26.68	33.0
Shanghai	2.30 ± 1.50	1.24 ± 0.90	3.37 ± 1.00	2.7
Vladivostok	6.21 ± 7.95	0.39 ± 0.20	12.03 ± 7.51	30.8
Busan	1.44 ± 1.01	0.36 ± 0.02	2.17 ± 0.25	6.0

[a] Annual = (summer + winter)/2.

Table 3. Annual $[P_h]$ and $[P_l]$ (μg m^{-3}) in 10 cities with $[P_h]/[P_c]$ ratios.

City	$[P_h]$	$[P_l]$	$[P_h]/[P_c]$
Sapporo	0.77 ± 0.75	0.38 ± 0.40	0.70
Kanazawa	1.65 ± 2.91	0.29 ± 0.18	0.85
Tokyo/Sagamihara	0.37 ± 0.25	0.15 ± 0.15	0.71
Kitakyushu	0.35 ± 0.32	0.68 ± 0.79	0.34
Shenyang	7.93 ± 6.62	18.88 ± 24.23	0.30
Beijing	3.03 ± 3.52	27.26 ± 31.77	0.10
Shanghai	1.57 ± 1.11	0.73 ± 0.66	0.68
Vladivostok	1.93 ± 3.00	4.28 ± 6.09	0.31
Busan	0.75 ± 0.51	0.69 ± 0.57	0.52

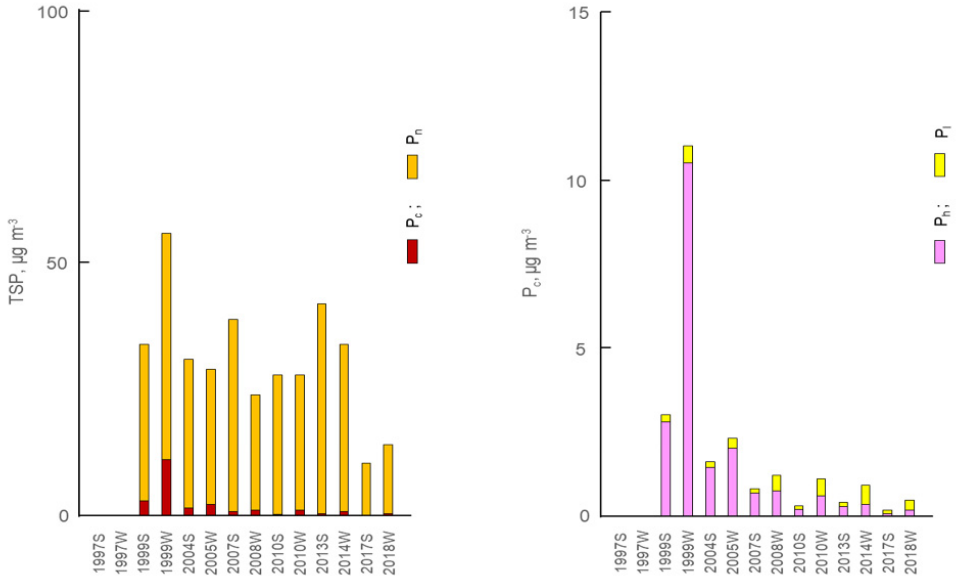

Figure 1. Sources of Atmospheric Total Suspended Particulate (TSP) and Combustion-Derived Particulates (P_c) in Kanazawa. P_c combustion-derived particulate matter; P_n non-combustion-derived particulate matter; P_h particulates from combustion sources with high-temperature; P_l particulates from combustion sources with low-temperature.

Figure 2 shows the profiles of [TSP] and $[P_c]$ in Kitakyushu. The levels of [TSP] and $[P_c]$ were similar to those in Kanazawa, but no decreasing trend was observed in $[P_c]$. This figure shows that $[P_l]$ was higher than $[P_h]$, which was different from Kanazawa (Figure 1). Table 3 shows that the $[P_h]/[P_c]$ ratio in Kitakyushu (0.34) was much smaller than the $[P_h]/[P_c]$ ratios in other Japanese cities (0.70–0.85). Considering that Kitakyushu is a typical steel manufacturing city (Table S1), these results suggest that coke oven plants, which consume large amounts of coal, were the main contributor to P_c. We collected TSP samples in Muroran, another steel manufacturing city in Japan, in our previous study [24]. The $[P_h]/[P_c]$ ratio of Muroran was much smaller (0.11), as calculated by the NP-method. These results suggest that coke oven plants were the main contributor to P_l. It should be emphasized that the annual $[P_c]$ in Kitakyushu was as low as the annual $[P_c]$ in the other Japanese cities. This result suggests that P_c was effectively removed from coke oven emissions through PM/sulfur oxides precipitators and filters [25].

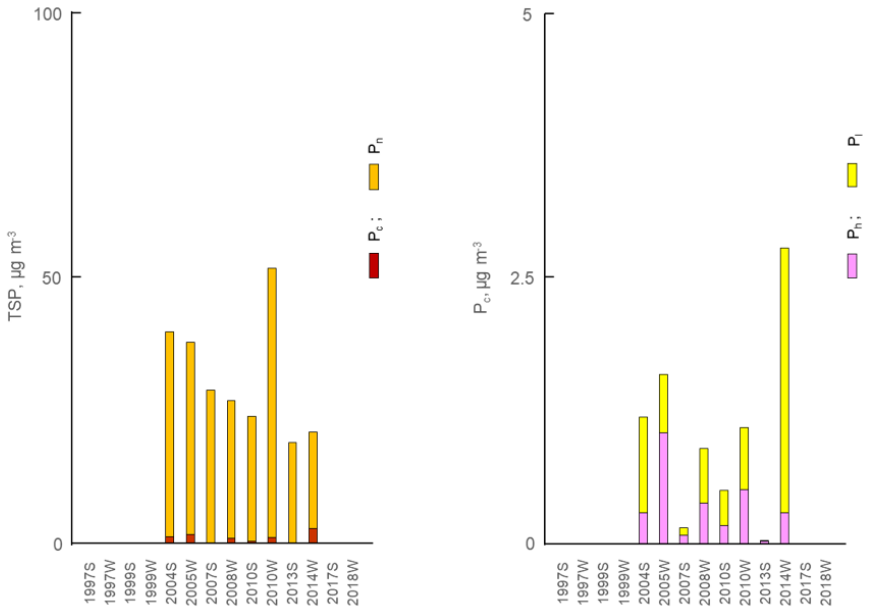

Figure 2. Sources of Atmospheric Total Suspended Particulate (TSP) and Combustion-Derived Particulates (P_c) in Kitakyushu. P_c, P_n, P_h, and P_l; The same as in Figure 1 caption.

Among the three Chinese cities, Shenyang and Beijing showed much higher winter [P_c] (more than 40 μg m^{-3}) than Shanghai (3.37 μg m^{-3}) (Table 2). This was reflected in higher [TSP] values (Table S1) and much larger y (=[P_c]/[TSP]) values in these two cities in winter than in summer (Table S3). Figure 3 shows the profiles of [TSP] and [P_c] in Beijing, where large seasonal changes (summer < winter) were observed in [P_c], as well as in the [P_c]/[TSP] ratio. The high winter [P_c] was mainly attributed to high [P_l]. In contrast to the large [P_l]/[P_c] ratio, the [P_h]/[P_c] ratio in Beijing (0.10) was much smaller than that in Shanghai (0.68) (Table 3). The [TSP] and [P_c] profiles in Shenyang and Vladivostok were similar to those in Beijing.

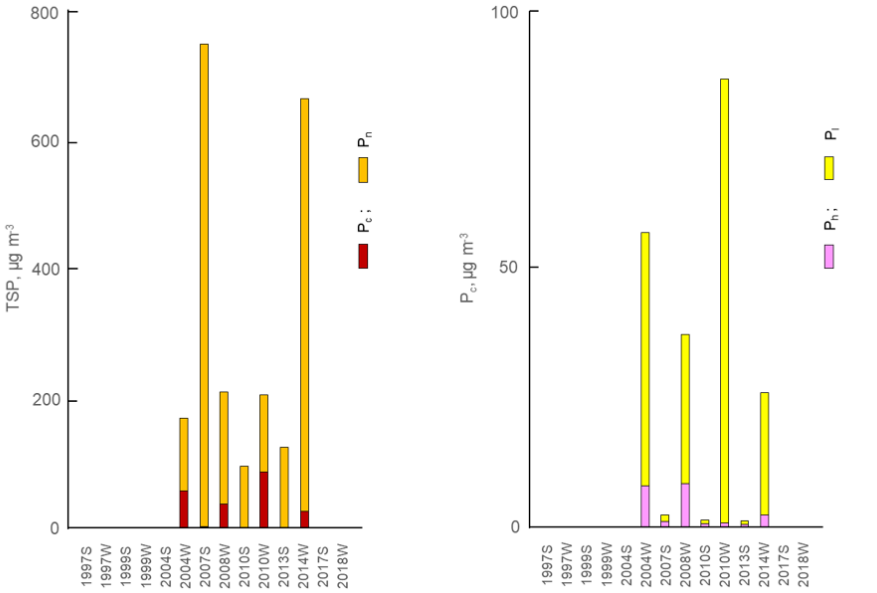

Figure 3. Sources of Atmospheric Total Suspended Particulate (TSP) and Combustion-Derived Particulates (P_c) in Beijing. P_c, P_n, P_h, and P_l; The same as in Figure 1 caption.

Figure 4 shows the [TSP] and [P_c] profiles in Shanghai, where the [P_c] level was as low as those in Japanese cities, and its seasonal changes were not as large as those in Beijing.

However, the $[P_h]/[P_c]$ ratio was much larger in Shanghai than in Beijing. Moreover, the winter to summer ratio of $[P_c]$ of Shanghai (2.7) was much smaller than that of Beijing (33.0) (Table 2). Considering that coal is consumed for winter heating in northern and central China and far eastern Russia, these results suggest that the high winter $[P_l]$ values in Shenyang, Beijing, and Vladivostok were ascribed to coal combustion for heating. In Shanghai, where winter heating is not used, the main contributor to P_c was vehicles. Thus, the Chinese cities differed significantly in the concentrations and sources of P_c.

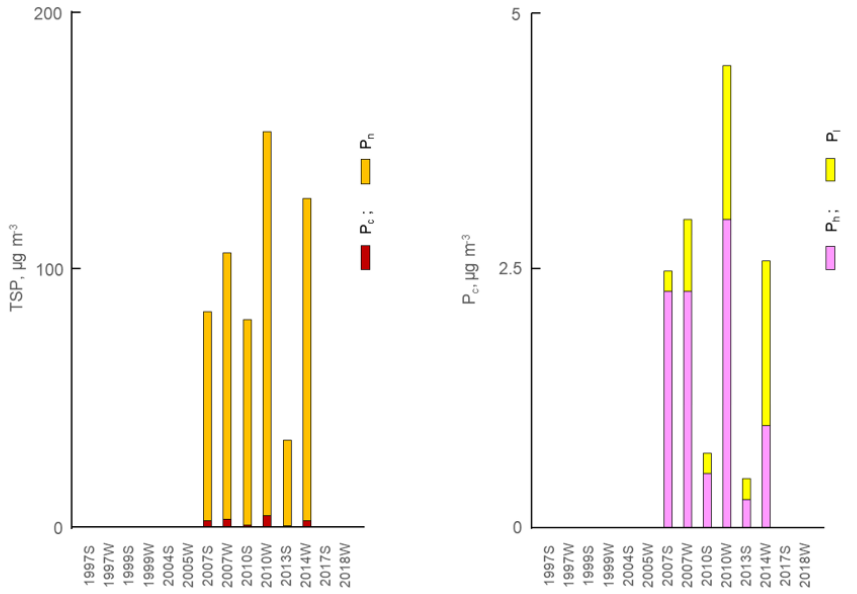

Figure 4. Sources of Atmospheric Total Suspended Particulate (TSP) and Combustion-Derived Particulates (P_c) in Shanghai. P_c, P_n, P_h, and P_l; The same as in Figure 1 caption.

$[P_c]$ concentrations in Busan were as low as those in Japanese cities, and changed little with season (Table 2), although the monitoring period was not long. The $[P_h]/[P_c]$ ratio (0.52) was close to the values of the Japanese cities with the exception of Kitakyushu (Table 3), suggesting that the main contributor to P_c was vehicles.

Based on their profiles of $[P_c]$, $[P_h]$ and $[P_l]$, the 10 cities were separated into three classes. Class 1: commercial cities whose major contributor to P_c was vehicles and which showed lower $[P_c]$ levels with larger $[P_h]/[P_c]$ ratios. Sapporo, Kanazawa, Tokyo, Sagamihara (Japan), Shanghai (China), and Busan (Korea) were contained in this class. Class 2: cities whose main source of P_c was coal heating which emits large amounts of P_l. This results in the much higher winter $[P_c]$ with larger $[P_l]/[P_c]$ ratios. Beijing, Shenyang (China), and Vladivostok (Russia) were contained in this class. Class 3: steel manufacturing city which showed lower $[P_c]$ with larger $[P_l]/[P_c]$ ratio. The low $[P_c]$ appeared to be due to elimination of P_l from coke oven plants. Only Kitakyushu was contained in this class. Thus, different long-term and seasonal changes in contributions of vehicles and coal combustion to urban atmospheric suspended particulate matter (TSP) in each city, that were unknown in our previous studies [10–12], have been elucidated.

3.2. Overall Trends of the Western Pacific

Oil and coal account for more than 60% of the world's primary energy production, around 30% of which was consumed in the Western Pacific countries in 2019 [23]. Therefore, this region has a strong effect on global atmospheric conditions. Figure 5 shows long-term trends of summer and winter $[P_c]$ in the Western Pacific from 1997 to 2018. $[P_c]$ levels in Sapporo, Kanazawa, Tokyo, Sagamihara, Shanghai, Kitakyushu, and Busan (Figure 5A) were low. Their first-order linear regression equations, based on the least squares method, show negative slopes (summer −0.117 and winter −0.282) and the correlation coefficients

(r) (−0.636 and −0.547, respectively) mean that the correlations were negative. [P_c] levels in Beijing, Shenyang, and Vladivostok (Figure 5B) were high. The first-order linear regression equation for winter shows a negative slope (−0.3643). The r value (−0.522) with p values smaller than 0.05 means that the correlation was negative. However, the summer equation has a very small r value (= 0.023) and p values larger than 0.05. In these cities, [P_l] was often relatively high even in summer (Table S2), suggesting that coal combustion such as from factories may decrease the correlation. These results suggest that [P_c] was decreasing in this region.

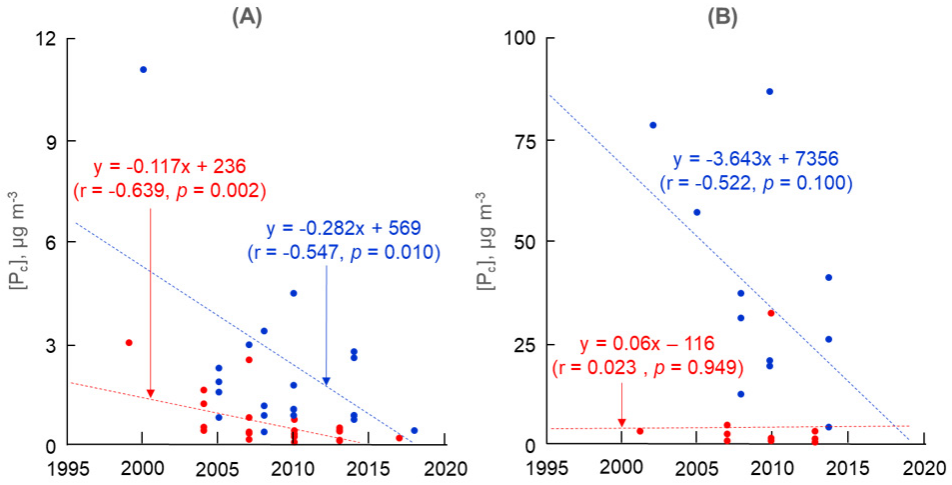

Figure 5. Long-Term Trends of Summer and Winter [P_c] in the Western Pacific. (**A**) Sapporo, Kanazawa, Tokyo, Sagamihara, Shanghai, Kitakyushu, Busan; (**B**) Beijing, Shenyang, Vladivostok. Season: ● Winter, ● Summer.

Coal and gasoline were considered to be the main combustion sources of P_c in this region in the last two decades [10]. Figure 6 shows the long-term trends of summer and winter [P_h]/[P_c] ratios of the 10 cities from 1997 to 2018. Figure 6A,B contain the same cities as Figure 5. Figure 6A shows first-order linear regression equations with negative slopes (summer −0.0201 and winter −0.0237) and negative r values (−0.487 and −0.546, respectively) with p values smaller than 0.05. Figure 6B shows the equations with negative slopes (summer −0.028 and winter −0.0072), although the correlations are not so strong as those in Figure 6A, and p values are larger than 0.05. These results indicate that P_c emission from vehicles was decreasing, but P_c emission from other sources, such as coal combustion, was not.

This is the first study to estimate the long-term and seasonal contributions of combustion sources to TSP in the Western Pacific cities. Many gasoline and diesel engine vehicles will be replaced by electric and hydrogen engines vehicles which do not emit P_c, but consumption of fuels for air and sea transportation is increasing [26]. Although there is a global trend to replace coal with natural gas and renewable energies, a quick shift may not be easy. More improvements of combustion systems for fuels will be needed to reduce emissions of P_c in this region.

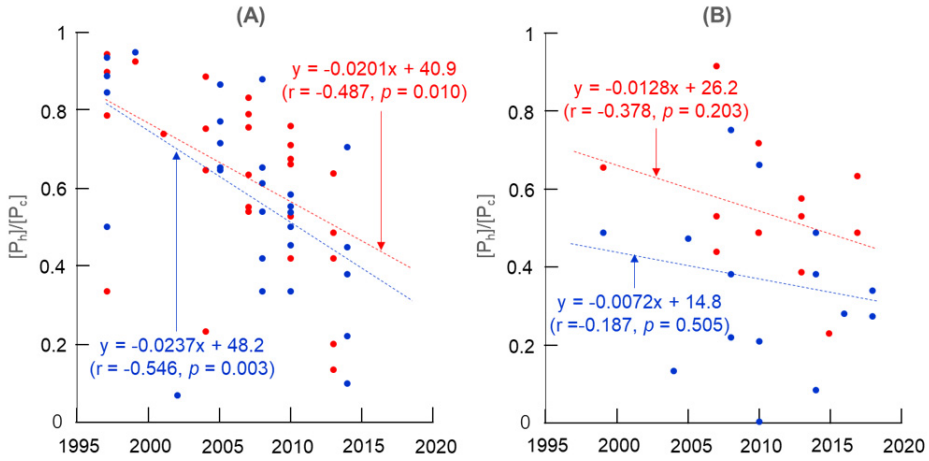

Figure 6. Long-Term Trends of Summer and Winter $[P_h]/[P_c]$ Ratios in the Western Pacific. (**A**) Sapporo, Kanazawa, Tokyo, Sagamihara, Shanghai, Busan, Kitakyushu; (**B**) Beijing, Shenyang, Vladivostok. Season: ● Winter, ● Summer. P_c, combustion-derived particulate P_h, P_c derived from combustion with high temperature.

4. Conclusions

In order to clarify long-term and seasonal change in contributions of vehicles and coal combustion to urban atmospheric suspended particulate matter (TSP) in the Western Pacific, combustion-derived particulates (P_c) in TSP collected in ten cities from 1997 to 2018 were analyzed using the NP method. The method separates P_c into particulates originating from high-temperature (P_h) and low-temperature (P_l) combustion sources. Using this method, ten cities in the Asia-Pacific region were separated into three classes.

Class 1: commercial cities whose major contributor to P_c was from vehicles and which showed lower $[P_c]$ values with larger $[P_h]/[P_c]$ ratios. Sapporo, Kanazawa, Tokyo, Sagamihara (Japan), Shanghai (China), and Busan (Korea) were contained in this class.

Class 2: cities whose main source of P_c was from coal heating, and which showed much higher winter $[P_c]$ with larger $[P_l]/[P_c]$ ratios. Beijing, Shenyang (China), and Vladivostok (Russia) were contained in this class.

Class 3: steel manufacturing city which showed lower $[P_c]$ with larger $[P_l]/[P_c]$ ratio. The low $[P_c]$ appeared to be due to the elimination of P_l from coke oven plants. Only Kitakyushu was contained in this class.

This study has elucidated the contribution of sources to urban atmospheric TSP in the Western Pacific which was previously unknown. Overall, $[P_c]$ was decreasing with seasonal difference in this region, mainly due to the decreasing contribution of vehicles to P_c, but not due to a decrease in coal combustion.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12042149/s1, Text S1: Determination of PAHs and NPAHs [27,28]; Figure S1: Sampling cities in Wesstern Pacific Ocean; Table S1: Characteristics of the sampled cities; Table S2: Atmospheric concentrations of TSP, 1-NP and Pyr in 10 cities from 1997 to 2018; Table S3: x and y values for 10 cities from 1997 to 2018.

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Abbreviations

TSP	total suspended particulate matter
PAHs	polycyclic aromatic hydrocarbons
NPAHs	nitropolycyclic aromatic hydrocarbons
P_c	combustion-derived particulate matter
P_n	non-combustion-derived particulate matter
P_h	particulate emitted from high-temperature combustion source
P_l	particulate emitted from low-temperature combustion source
Pyr_h	P_h-bound Pyr
Pyr_l	P_l-bound Pyr
$1\text{-}NP_h$	P_h-bound 1-NP
$1\text{-}NP_l$	P_l-bound 1-NP
ΣPAH	sum of fluoranthene, Pyr, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene and indeno [1,2,3-*cd*]pyrene
ΣNPAH	sum of 9-nitroanthracene, 1-NP, 6-nitrocrysene, 7-nitrobenz[*a*]anthracene, 3-nitroperylene and 6-nitrobenzo[*a*]pyrene

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